

AD-A074 055

COLORADO STATE UNIV FORT COLLINS DEPT OF CHEMISTRY  
TWO PHOTON SPECTROSCOPY OF PYRAZINE AND TRIAZINE.(U)

F/6 7/4

SEP 79 J D WEBB, K M SWIFT, E R BERNSTEIN

N00014-75-C-1179

UNCLASSIFIED

TR-22

NL

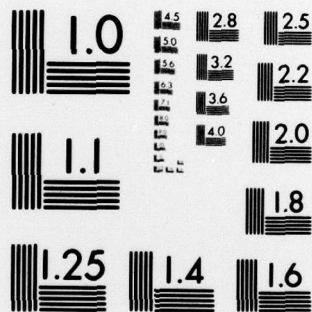
OF  
AD  
A074055



END  
DATE  
FILMED

10-79

DDC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

AD A 074055

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-1179

Task No. NR 056-607

TECHNICAL REPORT NO. 22

LEVEL

TWO PHOTON SPECTROSCOPY OF PYRAZINE AND TRIAZINE

by

J. D. Webb, K. M. Swift and E. R. Bernstein

DDC  
REF ID: A67112  
SEP 21 1979  
RESERVED

Prepared for Publication in  
Proceedings of 14th European Congress  
on Molecular Spectroscopy

Department of Chemistry  
Colorado State University  
Fort Collins, Colorado 80523

Sept 21 1979

Reproduction in whole or in part is permitted for  
any purpose of the United States Government.

Approved for Public Release; Distribution Unlimited.

79 09 20 013

404992

DDC FILE COPY

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 22	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "TWO PHOTON SPECTROSCOPY OF PYRAZINE AND TRIAZINE"		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. D. Webb, K. M. Swift and E. R. Bernstein		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-1179
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Colorado State University Fort Collins, Colorado 80523		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 056-607
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		12. REPORT DATE September 1979
		13. NUMBER OF PAGES 6
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for Public Release; Distribution Unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <div style="display: flex; justify-content: space-between;"> <div> nonlinear optics multiphoton absorption photochemistry pyrazine triazine </div> <div> photoacoustic spectroscopy vibronic coupling Jahn Teller effect pseudo Jahn Teller effect </div> </div>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>Two photon absorption spectra, detected by fluorescence, phosphorescence, and photoacoustic methods are presented for pyrazine and triazine. Vibronic assignments are made in both systems based on polarization and contour analysis. For pyrazine, origin intensity is observed which suggests the <math>(B_u)</math> state does not possess inversion symmetry. Linear, quadratic, and pseudo-Jahn Teller couplings are discussed for triazine.</p>		

DD FORM 1 JAN 73 1473

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

## TWO PHOTON SPECTROSCOPY OF PYRAZINE AND TRIAZINE

J. D. WEBB, K. M. SWIFT and E. R. BERNSTEIN

Colorado State University, Department of Chemistry, Fort Collins, Colorado  
80523 (U.S.A.)

### ABSTRACT

Two photon absorption spectra, detected by fluorescence, phosphorescence, and photoacoustic methods are presented for pyrazine and triazine. Vibronic assignments are made in both systems based on polarization and contour analysis. For pyrazine, origin intensity is observed which suggests the  $16_{\text{Su}}$  state does not possess inversion symmetry. Linear, quadratic, and pseudo-Jahn Teller couplings are discussed for triazine.

### INTRODUCTION

Multiphoton spectroscopy has recently received a good deal of attention, particularly with regard to its application to molecular systems (ref. 1). The motivations behind such investigations of typically well studied systems (e.g., benzene and pyrazine) are: new selection rules allow photophysical and photochemical studies of different excited electronic and vibronic states; multiphoton transitions may reach vacuum ultraviolet regions with high resolution and relative ease; it is possible to obtain polarized spectra (with linearly and circularly polarized photons) even in isotropic liquids and gases; using counter propagating beams, Doppler free high resolution gas phase spectra can be observed; intense electric dipole transitions in bulk materials can be more easily studied; and infrared multiphoton photochemistry, photophysics, and isotope separation can be pursued.

As with most laser spectroscopic techniques it turns out to be most useful to use what may be called secondary detection techniques; that is, it is not the loss of photons from the laser beam that is monitored during an experiment, but some ensuing molecular process (i.e., emission of photons, sound or heat pulses, or electrons). In this work we use fluorescence, phosphorescence, and photoacoustic techniques to detect the primary (two photon) absorption process.

The systems studied are 1-10 torr of pyrazine and triazine. Both of these molecules are relatively well studied over the past 25 years because of their general interest for N-heterocyclic photochemistry and photophysics.

Acceleration for	
NTIS Grant	<input checked="checked" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist	Availand/or special
A	

( $D_{3h}$  symmetry--symmetric top) has dipole forbidden (two photon allowed)  $1,3E''$  first excited states. Strong vibronic (inter- and intra-state) coupling is expected for both these states. Location of  $n\pi^*$  and  $\pi\pi^*$  excited states and determination of their geometry is essential for an understanding of the series. Pyrazine ( $D_{2h}$  symmetry--asymmetric top) has a  $1B_{3u}$  first excited singlet state which is vibronically allowed in two photon spectra. Aside from the general interest in vibronic structure and geometry of this system, the location of other  $n\pi^*$  states, particularly the two photon allowed  $1B_{2g}$  arising from  $n(b_{1u})$  and  $\pi(b_{3u})$  orbitals, has been of long-standing interest and considerable importance.

In the following section is presented a brief discussion of experimental techniques. In Section III, results and their interpretation are given. Analysis of these data is at present somewhat tentative, due to the occurrence of strong intrastate vibronic coupling (linear Jahn Teller - LJT, quadratic Jahn Teller - QJT effects) and interstate vibronic coupling (pseudo Jahn Teller - PJT effect). A more complete and detailed analysis will rely heavily on calculations (similar to those on transition metal hexafluorides - ref. 2) and contour simulations presently in progress.

For this paper we discuss assignments, nature and source of vibronic interactions, and qualitative features of geometry and symmetry that are apparent from the spectra.

#### EXPERIMENTAL

Samples were vacuum distilled through molecular sieve to remove all traces of water and air. Triazine was fused with potassium prior to distillation. Three different detection methods were employed for these experiments but all had the general design given in Figure 1. Fluorescence detection apparatus was the same as

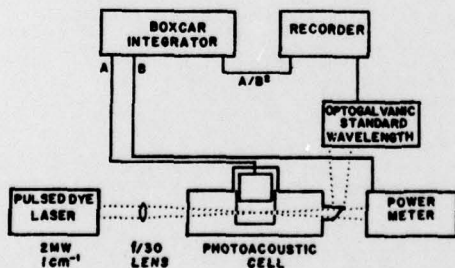


Fig. 1. Experimental apparatus for multiphoton spectroscopy photoacoustically detected. For emission detection, the microphone is replaced with photomultiplier tube.

the photoacoustic depicted with the microphone replaced with a cooled RCA 8850 phototube. Phosphorescence times were long enough to employ digital boxcar techniques with photon counting. Spectra are calibrated to  $0.1 \text{ cm}^{-1}$  with the optogalvanic effect using an Fe-He hollow cathode lamp.

## RESULTS AND DISCUSSION

### Pyrazine

We begin discussion of results with pyrazine because they are more simple to analyze. Figure 2 shows a portion of the two photon spectrum of pyrazine photoelectrically detected. Well developed, rather broad contours obtain. The major

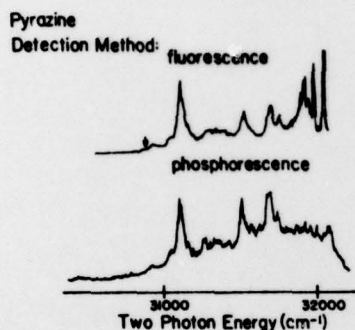


Fig. 2. Pyrazine two photon spectra of  $^1B_{3u}$  state. Photoelectrically detected; origin marked with arrow.

fluorescence signal is due to CN (cyanide) emission. This diatomic radical is created photochemically following pyrazine two photon absorption. The large signal at about  $32,000 \text{ cm}^{-1}$  is due to two photon absorption of ground state CN followed by fluorescence. Polarized higher resolution photoacoustically detected spectra presented in Figure 3 (which do not evidence CN) show totally symmetric peaks due to  $b_{3u}$  vibrations ( $16b_0^1$  and  $11b_0^1$ ). This figure shows origin intensity which is unpolarized. Spectra taken at  $100^\circ\text{C}$  do not show any increase or variation in this intensity relative to other features; thus it is probably not sequence structure. We tentatively conclude that this is origin intensity and therefore the molecule has lost its inversion symmetry in the  $^1B_{3u}$  state.

A thorough search for the  $^1B_{2g}$  state  $1000 \text{ cm}^{-1}$  to lower energy than the 0-0 transition of  $^1B_{3u}$  and up to  $2000 \text{ cm}^{-1}$  to higher energy than the 0-0 gave no hint of this two photon allowed state.

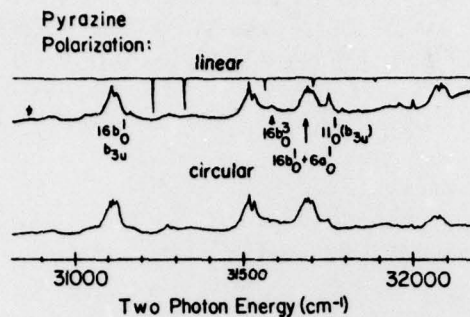


Fig. 3. Same as Figure 2 but polarized and photoacoustically detected, origin marked with arrow.

#### Triazine

Triazine represents a far more complicated situation than does pyrazine due to strong Jahn Teller coupling (e.g., e' modes  $\nu_6$  and  $\nu_8$ ) and strong pseudo Jahn Teller (e.g., e' modes and e'' modes  $\nu_{10}$  and  $\nu_{16}$ ). This situation obtains, of course, because of the degenerate electronic state E'' and the increased density of the excited electronic manifold ( $A_1'$ ,  $A_2'$ , E''  $n\pi^*$  states and  $A_1'$ ,  $A_2'$ , E'  $\pi\pi^*$  states).

Figure 4 presents a comparison of the one and two photon spectra of this molecule. Notice in particular that there is little overlap between the two spectra even though  $D_{3h}$  selection rules indicate many coincidences should be present. Most importantly, however, the E'' (perpendicular) origin is observed and assigned based

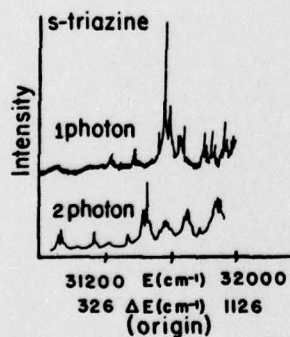


Fig. 4. Sym-triazine E'' spectra.

on its contour which was matched with computer simulation. Again, CN emission can be used to detect the absorption photoelectrically; photoacoustic detection shows small intensity differences between the two techniques. Detailed polarization studies (Figure 5) allow  $e''$  modes  $10_0^1$  ( $430\text{ cm}^{-1}$ ) and  $16_0^1$  ( $300\text{ cm}^{-1}$ ) to be

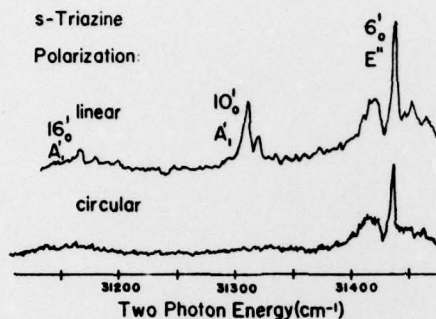


Fig. 5. Polarized, photoacoustically detected portion of triazine spectrum.

identified. These have been shifted from their ground state values ( $340$  and  $1031\text{ cm}^{-1}$ ) and split due to PJT coupling with  $\pi\pi^*$  states of  $A_1'$ ,  $A_2'$ , or  $E'$  symmetry.

The origin and  $6_0^1$  ( $e'$ ) at  $550\text{ cm}^{-1}$  have the same contour (Figure 6) and polarization behavior and are identified as  $E''$  vibronic components of JT active modes.

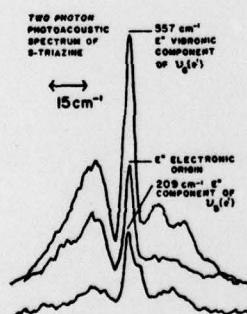


Fig. 6. Comparison of three  $E''$  vibronic features ( $E'' \times e'$ ) in the triazine spectrum.

When compared to the one photon spectra in Figure 4, the other  $6_0^1$  component ( $A_2'^1$ ) is located at  $670\text{ cm}^{-1}$ . Such a splitting is inconsistent with LJT coupling in sign and can only arise through: a) PJT coupling; b) QJT coupling; c) strong

mixing of e' modes. The precise mechanism for such strong higher order effects is presently under consideration but is not without precedent (refs. 3, 4).

Finally the feature at  $200\text{ cm}^{-1}$  (Figure 6) is similar to the origin and  $6_0^1$  (E'') in contour and polarization behavior leading one to assign it as an e' vibration. A tentative assignment for this feature is  $8_0^1$  ( $\nu_8''$  (e')  $1570\text{ cm}^{-1}$ ). Such a large change in frequency upon excitation would be due to PJT coupling as is found in  $^3B_{1u}$   $8_0^1$  of  $C_6H_6$  (refs. 3,4) ( $\nu_8$   $340\text{ cm}^{-1}$  while  $\nu_8''$   $1595\text{ cm}^{-1}$ ). The PJT coupling would take place with E'',  $A_2''$ , or  $A_1''$   $D_{3h}$   $\pi\pi^*$  electronic states. Again this assignment must be viewed as tentative pending completion of confirming vibronic coupling and contour calculations.

#### CONCLUSIONS

It is clear from the discussion, as well as the presented figures, that phosphorescence, fluorescence, and photoacoustic detection are all applicable to two photon spectroscopy. Different detection techniques emphasize different aspects of molecular photophysical and photochemical processes. For pyrazine it is possible to observe two photon spectra by all three techniques but for fluorescence detection cyanyl (CN) emission was the major component of the signal. A number of vibrations are assigned based on polarized spectra and known coincidences. Apparent non-hot band intensity at the origin of the  $^1B_{3u}$  state indicates that this state may have lost its inversion symmetry. The E'' origin of the first excited singlet state of triazine was located and assigned. Vibronic states  $16_0^1$  (e'') and  $10_0^1$  (e'') were identified by polarization studies; both modes are shifted and split by PJT coupling with  $\pi\pi^*$  states. JT active e' modes were assigned:  $6_0^1$  (E'' component) is placed at  $560\text{ cm}^{-1}$  with its  $6_0^1$  ( $A_2''$  component) partner at  $660\text{ cm}^{-1}$ ; and  $8_0^1$  (E'' component) highly perturbed is tentatively suggested to lie at about  $200\text{ cm}^{-1}$  above the  $^1E''$  origin.

#### ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research, and Army Research Office-Durham.

#### REFERENCES

1. a) W. M. McClain, R. A. Harris, *Excited States*, Ed. E.C. Lim, Academic Press, III (1977)1; b) R. M. Hochstrasser, H. N. Sung, J.E. Wessel, *J. Chem. Phys.* **60**(1974)317; c) K.M. Chen, E.S. Yueng, *J. Chem. Phys.* **69**(1978)43; d) F. Metz, et al., *Proc. Roy. Soc. Lond.* **A363**(1978)381; e) P. Esherick et al. *Chem. Phys.* **10** (1975)415; f) R.A. Hochstrasser et al. *J. Chem. Phys.* **70**(1979)870.
2. E. R. Bernstein and J.D. Webb, *Mol. Phys.* **36**(1978)1113; *ibid.* **37**(1979)191,203,1509, and references therein.
3. J. H. van der Waals, A.M.D. Berghuis and M.S. de Groot, *Mol. Phys.* **13**(1967)301; **21**(1971)497; and J. van Egmond and J. H. van der Waals, *Mol. Phys.* **28**(1974)457.
4. D. M. Burland, G. Castro and G. W. Robinson, *J. Chem. Phys.* **52**(1970)4100.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	U.S. Army Research Office P.O. Box 1211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Weapons Center China Lake, California 93555 Attn: Dr. A. B. Amster Chemistry Division	1
ONR Area Office One Hallidie Plaza, Suite 601 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Naval Civil Engineering Laboratory Port Hueneme, California 93401 Attn: Dr. R. W. Drisko	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Professor K. E. Woehler Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1	Naval Ship Research and Development Center Annapolis, Maryland 21401 Attn: Dr. G. Bosmajian Applied Chemistry Division	1
		Naval Ocean Systems Center San Diego, California 91232 Attn: Dr. S. Yamamoto, Marine Sciences Division	1

End

TECHNICAL REPORT DISTRIBUTION LIST, 051A

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. M. A. El-Sayed University of California, Los Angeles Department of Chemistry Los Angeles, California 90024	1	Dr. M. Rauhut American Cyanamid Company Chemical Research Division Bound Brook, New Jersey 08805	1
Dr. M. W. Windsor Washington State University Department of Chemistry Pullman, Washington 99163	1	Dr. J. I. Zink University of California, Los Angeles Department of Chemistry Los Angeles, California 90024	1
Dr. E. R. Bernstein <del>Colorado State University</del> <del>Department of Chemistry</del> Fort Collins, Colorado 80521	1	Dr. B. Schechtman IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1	Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. J. R. MacDonald Naval Research Laboratory Chemistry Division Code 6110 Washington, D.C. 20375	1		
Dr. G. B. Schuster University of Illinois Chemistry Department Urbana, Illinois 61801	1		
Dr. E. M. Eyring University of Utah Department of Chemistry Salt Lake City, Utah	1		
Dr. A. Adamson University of Southern California Department of Chemistry Los Angeles, California 90007	1		
Dr. M. S. Wrighton Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1		